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Dear Bolko,

This is the third quarterly report of our project under the current Thin Film Partnership Program (Subcontract No. XXL-5-44205-12 to University of Nevada, Las Vegas: Characterization of the electronic and chemical structure at thin film solar cell interfaces). A brief summary and details of our activities are given below. This report is in fulfillment of the deliverable schedule of the subcontract statement of work (SOW).

Summary

This project is devoted to deriving the electronic structure of interfaces in Cu(In,Ga)(S,Se)_2 and CdTe thin film solar cells. By using a unique combination of spectroscopic methods (photoelectron spectroscopy, inverse photoemission, and X-ray absorption and emission) a comprehensive picture of the electronic (i.e., band alignment in the valence and conduction band) as well as chemical structure can be painted. The work focuses on (a) deriving the bench mark picture for world-record cells, (b) analyze state-of-the-art cells from industrial processes, and (c) aid in the troubleshooting of cells with substandard performance.

In our last beamtime at the Advanced Light Source, Lawrence Berkeley National Laboratory, we conducted first XES measurements of CdTe/CdS samples prepared by the group of A. Compaan (University of Toledo). Furthermore, we continued the evaluation of the XES/PES data of the Cu(In,Ga)Se_2 samples (provided by NREL) already described in the last quarterly report. A new electron analyzer was delivered and installed in our surface spectroscopy system at UNLV; the commissioning is currently under way.

Detailed Description of the Activities:

1. Investigation of CdTe/CdS samples from Univ. Toledo

In our last beamtime at the Advanced Light Source, Lawrence Berkeley National Laboratory (Nov. 2 – 13, 2005), we conducted first XES measurements of CdTe/CdS samples prepared by the group of A. Compaan (University of Toledo). These investigations were based on

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two sets of samples, namely differently treated CdS thin films and CdTe/CdS thin film stacks, respectively. For the latter set of samples, the impact of CdCl₂-treatment on the CdTe/CdS thin film stacks was investigated, while for the CdS thin films also the influence of Cu-diffusion was analyzed. In addition, some powder samples (CdS, CdSO₄, CdCl₂) were characterized for comparison.

In total, we thus investigated eight different samples:

Sample	Treatment	Name in the following text
CdS (thin film on glass)	none	as-grown CdS
CdS (thin film on glass)	CdCl ₂ -treated	CdCl ₂ -treated CdS
CdS (thin film on glass)	Cu-diffused	Cu-diffused CdS
CdTe/CdS (thin film stack on glass)	none	as-grown CdTe/CdS
CdTe/CdS (thin film stack on glass)	CdCl ₂ -treated	CdCl ₂ -treated CdTe/CdS
CdSO ₄ , CdS, CdCl ₂ (powders)	N/A	CdSO ₄ , CdS, CdCl ₂ references

All samples were investigated by X-ray emission spectroscopy (XES). This technique provides detailed informations about the chemical properties of the investigated samples. XES as a photon-in photon-out technique probes the “near-surface” bulk. In our case, where we have focused on the S L_{2,3} and Cl L_{2,3} emission, this method has an information depth of about 100 nm.

Fig. 1 (left) shows the S L_{2,3} XES spectra of the set of CdS samples. At first sight, all spectra look identical. The main feature (1) at 147.3 eV (which is actually a doublet indicated by the clearly visible shoulder at 149 eV) can be ascribed to S 3s electrons decaying into S 2p_{1/2} and S 2p_{3/2} core holes. In addition, the two peaks at 150.5 eV and 151.8 eV (2) correspond to Cd 4d electrons decaying into the S 2p_{1/2} and S 2p_{3/2} core holes, respectively, and thus indicate sulfur atoms bound to Cd. Furthermore, we observe the upper valence band of CdS at about 156 eV. Altogether, all spectra show the typical features of a S L_{2,3} spectrum of CdS, which is also confirmed by the respective spectrum of the CdS reference. However, a close inspection of the data shows small but significant differences for, e.g., the S L_{2,3} XES spectrum of the as-grown CdS (a) compared to that of the Cu-diffused CdS sample (b) (Fig. 2). The corresponding difference spectrum is also shown. The comparison of the (enlarged) difference (a)-(b) with a CdS and a CdSO₄ reference

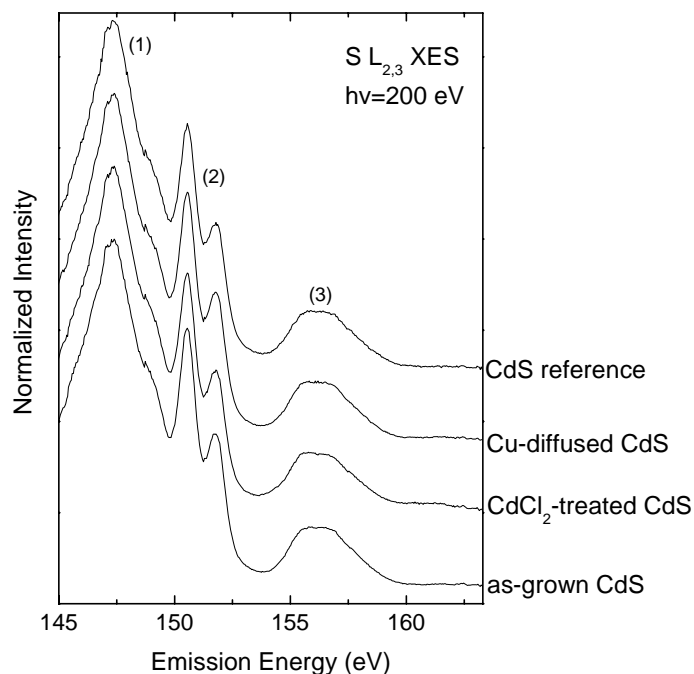


Fig. 1 S $L_{2,3}$ XES spectra of a set of differently treated CdS thin films. In addition, a corresponding spectrum of a CdS reference is also shown (top spectrum). The main features are labeled (1) – (3).

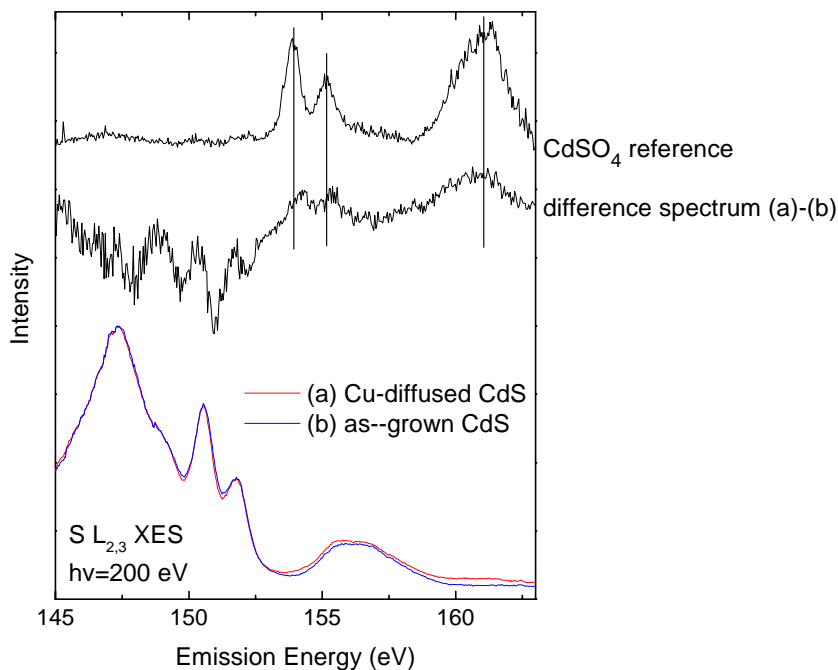


Fig. 2 S $L_{2,3}$ XES spectra of a Cu-diffused CdS thin film (a) plotted upon that of an as-grown CdS sample (b). In addition, the corresponding (enlarged) difference spectrum (a-b) and a CdSO₄ reference spectrum is also shown.

spectrum reveals that the features in the difference spectrum can be ascribed to the formation of S-O bonds and a localization of the Cd 4d-derived band.

The spectra of the differently treated CdTe/CdS thin film stacks are shown in Fig. 3. Since the thickness of the CdTe layer, which covers the CdS, is significantly beyond the information depth of the XES, one would not expect to observe a S $L_{2,3}$ signal; as shown for the as-grown CdTe/CdS thin film stack. However, the S $L_{2,3}$ spectrum of the CdCl₂-treated CdTe/CdS sample shows clearly some small (note the magnification factor) spectral features, which are similar to spectra shown in Fig. 1. A comparison with the spectrum of the as-grown CdS thin film as well as with the CdSO₄ reference reveals that the S $L_{2,3}$ spectrum of the CdCl₂-treated CdTe/CdS thin film stack can be described as a superposition of spectral features of both reference samples. Most prominently, the two peaks at 150.5 eV and 151.8 eV directly indicate S-Cd bonds, and the peaks at 153.9 eV, 155.1 eV, and 161.0 eV can be directly ascribed to S-O bonds. In consequence, this points to a CdCl₂-treatment-induced crack formation of the CdTe layer or to a strong intermixing (the latter is commonly accepted in the community). For the CdTe/CdS thin film stacks we also investigated the Cl $L_{2,3}$ XES spectra, as shown in Fig. 4 (multiplied by the given magnification factors). The two major features of the observed spectra at 182.3 eV and 183.8 eV can again be ascribed to 3s electrons decaying into the 2p_{1/2} and 2p_{3/2} core holes, this time only for Cl. As expected, we find a Cl $L_{2,3}$ XES spectrum for the CdCl₂-treated CdTe/CdS sample (middle spectrum in Fig. 4), the main features of which are quite similar to those of a CdCl₂ reference. The fact that the structures between 185 and 190 eV and between 190 eV and 194 eV are less pronounced than in the

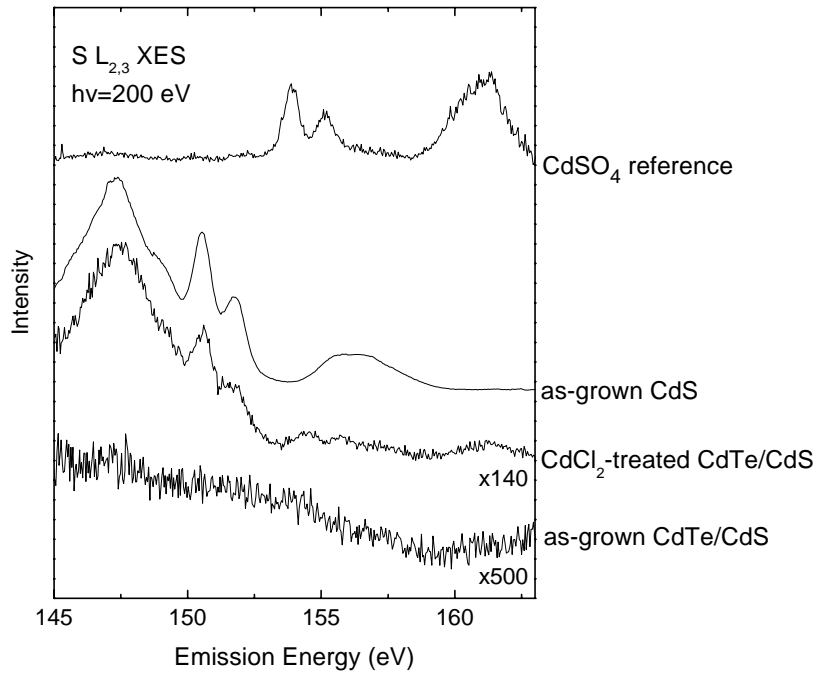


Fig. 3 S $L_{2,3}$ XES spectra of a set of differently treated CdTe/CdS thin film stacks. In addition, the corresponding spectrum of an as-grown CdS thin film and a CdSO₄ reference spectrum are also shown. Note the different magnification factors.

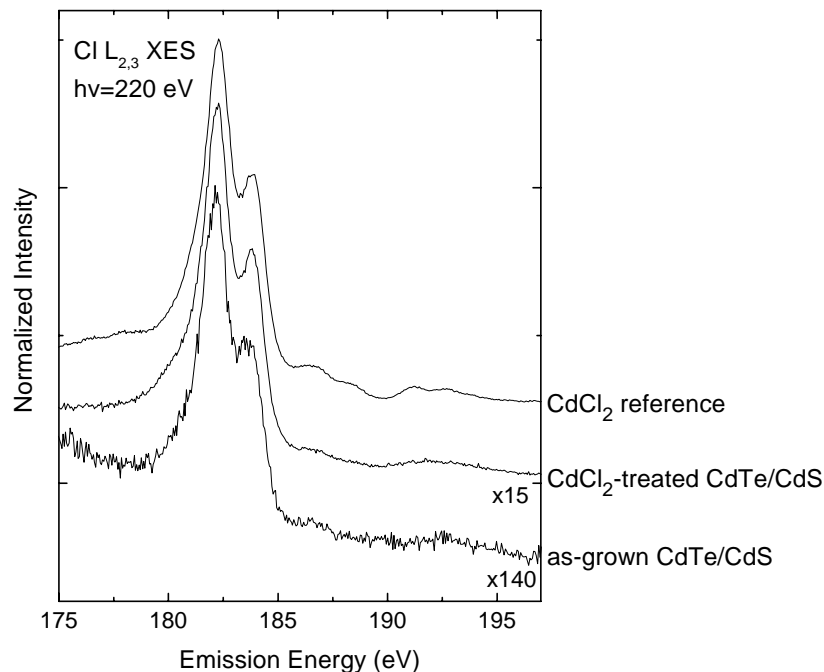


Fig. 4 Cl $L_{2,3}$ XES spectra of a set of differently treated CdTe/CdS thin film stacks. In addition, the corresponding spectrum of CdCl₂ reference spectrum is also shown. Note the different magnification factors.

reference sample, indicates the presence of Cl atoms that are not directly bound to Cd. Surprisingly, one can also identify a weak (note the magnification factor) Cl $L_{2,3}$ XES spectrum for the as-grown CdTe/CdS thin film stack, which shows all the characteristics of CdCl₂. Whether this is due to extrinsic contamination or an result of the used sample preparation (and thus significant) is the topic of future experiments.

Based on these results, we will continue the investigation of CdTe/CdS samples and extend them by investigating customized sample series with UPS and IPES to get insight into the band alignments at the various interfaces of the device structure of an CdTe-based solar cell. At the recent CdTe R&D team meeting (as well as at the CIS R&D team meeting) we have initiated a sample exchange with several (six) groups from within the Thin Film Photovoltaic Partnership Program. The planned experiments will shed light on the various interfaces in both CIS and CdTe cells. First samples have already been received at UNLV.

2. Replacement of the old electron analyzer

With funds from a different project, we were able to replace the old ESCALab MkII electron analyzer of the surface/interface characterization system at UNLV by a high-performance state-of-the-art instrument (SPECS PHOIBOS150 MCD). Currently, the commissioning of the new analyzer is under way. The increased resolution and an expected improvement of signal-to-noise ratio in XPS by about two orders of magnitude will greatly benefit the XPS and UPS results of our project.

If you have any questions, please do not hesitate to call me at (702) 895-2694.

Sincerely,

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CC: C. Lopez